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Multicomponent Micropatterns of Carbon Nanotubes

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Abstract

The excellent optoelectronic, mechanical, and thermal properties of carbon nanotubes have made them very attractive for a wide range of potential applications. However, many applications require the growth of aligned/micropatterned carbon nanotubes. Based on our previous work on the aligned and micropatterned growth of carbon nanotubes, we have recently developed a novel approach towards the micropattern construction of *perpendicularly-aligned* carbon nanotubes by simply pressing a Scotch tape pre-patterned with a non-adhesive layer onto a non-patterned aligned carbon nanotube film, followed by peeling off the Scotch tape from the quartz substrate in a dry state. In conjunction with the region-specific surface modification, this dry contact transfer method has enabled us to produce various multicomponent carbon nanotube micropatterns in which different components are interposed in an intimate fashion. Examples include micropatterns with self-assembled non-aligned carbon nanotubes interdispersed into the discrete areas in the patterned structure of aligned carbon nanotubes and flexible polymer films with embedded aligned carbon nanotube networks. More recently, we have also developed a simple but effective *template-free* electroplating method for region-selective deposition of cobalt and nickel nanoparticles for patterned growth of carbon nanotubes. These carbon nanotube micropatterns in which multicomponents are interposed in a controllable fashion should be of significance to many nanotube based multifunctional systems.

Keywords: Carbon nanotube, Alignment, Micropatterning, Electrodeposition, Multicomponent micropatterns, Polymer, Nanocomposite film.

1. Introduction

The recent development of nanotechnology has opened up novel fundamental and applied frontiers in materials science and engineering. At the nanometer scale, the wave like properties of electrons inside matter and atomic interactions are influenced by the size of the material [1]. As a consequence, changes in the size-dependent properties (*e.g.* melting points, magnetic, optic, and electronic properties) may be observed even without any compositional change [1]. Due to the high surface-to-volume ratio associated with nanometer-sized materials, a tremendous improvement in chemical properties is also achievable through the reduction in size [1]. Besides, new phenomena, such as the confinement-induced quantization effect, could also occur when the size of materials becomes comparable to the deBroglie wavelength of charge carriers inside [1].

By creating nanostructures, therefore, it is possible to control the fundamental properties of materials through the surface/size effect(s). This should, in principle, allow us to develop new materials and advanced devices of desirable properties and functions for numerous applications.

The recent discovery of carbon nanotubes [2] has opened up a new era in material science and nanotechnology. The interesting electronic and photonic properties, coupled with their unusual molecular symmetries, have made carbon nanotubes very attractive for many potential applications, including as new materials for electron field emitters in panel displays, single-molecular transistors, scanning probe microscope tips, gas and electrochemical energy storage, catalyst and protein/DNA supports, molecular-filtration membranes, and artificial muscles [3].

For most of the above-mentioned, and many other, applications, it is highly desirable to prepare aligned / micropatterned carbon nanotubes. We have previously prepared large-scale aligned multi-wall carbon nanotube arrays *perpendicular* to the substrate surface by pyrolysis of iron(II) phthalocyanine onto the pristine quartz glass plates [4]. Subsequently, we have also developed microfabrication

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methods for patterning the aligned carbon nanotubes with a sub-micrometer resolution and for patterned/non-patterned transferring such nanotube arrays to various other substrates of particular interest (*e.g.* polymer films for organic optoelectronic devices or metal substrates for electrochemistry) [4-8]. We have recently developed a novel approach towards the micropattern construction of *perpendicularly-aligned* carbon nanotubes by simply pressing a Scotch tape pre-patterned with a non-adhesive layer onto a non-patterned aligned carbon nanotube film, followed by peeling off the Scotch tape from the quartz substrate in a dry state. In conjunction with the region-specific surface modification, this dry contact transfer method has enabled us to produce various multicomponent carbon nanotube micropatterns in which different components are interposed in an intimate fashion. For example, micropatterns with self-assembled non-aligned carbon nanotubes interdispersed into the discrete areas in the patterned structure of aligned carbon nanotubes and flexible polymer films with embedded aligned carbon nanotube networks have been prepared. More recently, we have also developed a simple but effective *template-free* electroplating method for region-selective deposition of cobalt and nickel nanoparticles for patterned growth of carbon nanotubes. The dry contact transfer and template-free electroplating methods towards multicomponent carbon nanotube micropatterns should have important implications to many nanotube based multifunctional systems. In this paper, we will summarize our recent work on the mulitcomponent micropatterning of carbon nanotubes, along with some discussion on their potential applications.

2. Synthesis and micropatterning of aligned carbon nanotubes

Although carbon nanotubes synthesized by most of the common techniques, such as arc discharge and catalytic pyrolysis, often exist in a randomly entangled state (Fig. 1a) [3], aligned carbon nanotubes have been prepared either by post-synthesis fabrication or by synthesis-induced alignment [9]. In this regard, we have prepared aligned carbon nanotubes by pyrolyzing FePc and the detailed procedures for the aligned nanotube growth have been reported previously [10, 11]. Without repetition of detailed discussions on the synthesis and structural characterization, a typical Scanning Electron Microscopic (SEM) image of the FePc-generated aligned carbon nanotube array after having been transferred onto a gold foil is shown in Fig. 1b. As can been seen, the constituent nanotubes in the perpendicularly aligned carbon nanotube array have a fairly uniform length (*ca.* 10 μm). Elsewhere, we have also demonstrated that these aligned carbon nanotubes possess a graphitized structure with *ca.*50 concentric carbon shells and an outer diameter of *ca.*40 nm [12].

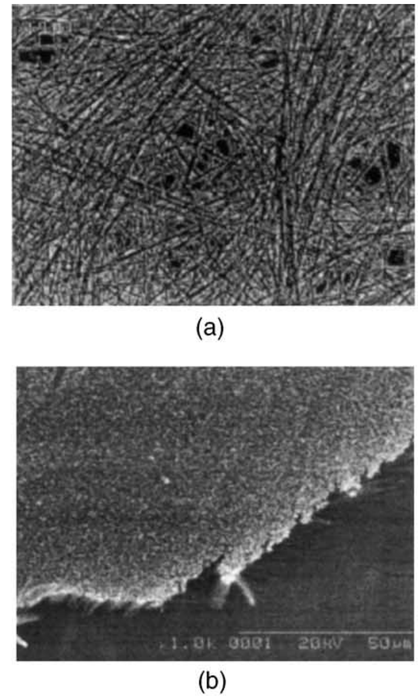
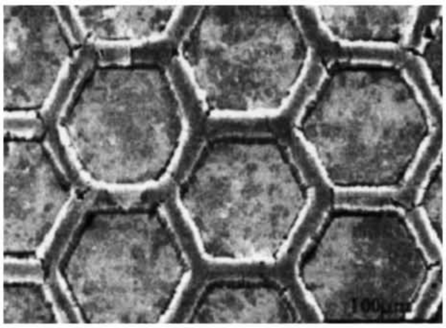


Fig. 1. (a) A typical TEM image of an oxidation-purified carbon nanotube sample generated by the arc discharge method. (b) A typical SEM image of the aligned carbon nanotube arrays prepared by pyrolysis of FePc.

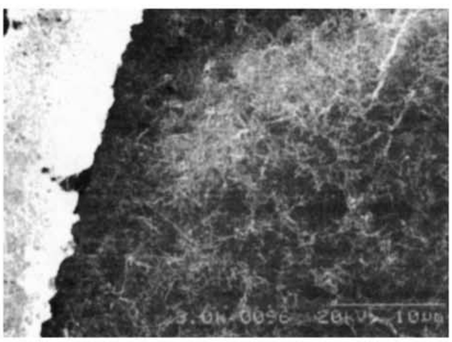
Apart from the aligned carbon nanotubes described above, certain applications (*e.g.* electron emitters for panel display, sensor arrays) may require the carbon nanotubes to be patterned onto various substrates, in a similar fashion as silicon or metals in semiconducting devices. On our further investigation of the aligned carbon nanotubes produced by the pyrolysis of FePc, we, among others, have recently developed a novel method for photolithographic generation of the perpendicularly-aligned carbon nanotube arrays with resolutions down to a micrometer scale [9].

In our further investigation on the microfabrication of aligned carbon nanotubes produced by the pyrolysis of FePc, we have recently found that micropatterns of the *perpendicularly-aligned* carbon nanotubes can be prepared by simply pressing a Scotch tape pre-patterned with a non-adhesive layer onto the FePc-generated carbon nanotube film, followed by peeling off the nanotubes together with the Scotch tape from the quartz substrate in a dry state (designated as: *dry contact transfer*). The dry contact transfer could not only maximize the retention of the structural integrity of the perpendicularly aligned carbon nanotubes after the contact transfer but also allow the region-specific interposition of other component(s) into the discrete areas interdispersed in the patterned nanotube structure.

In particular, we have prepared multicomponent interposed carbon nanotube micropatterns by the dry contact transfer of the FePc-generated perpendicular-aligned carbon nanotubes onto a Scotch tape pre-patterned with a thin layer of heptylamine-plasma-treated silver, followed by region-specific adsorption of acid-oxidized carbon nanotubes [13] onto the plasma-treated areas interdispersed in the patterned nanotube structure (Fig. 2a). As shown in Fig. 2b, both the contact transferred aligned carbon nanotubes and the adsorbed non-aligned carbon nanotubes are well registered into their respective areas.



(a)



(b)

Fig. 2. SEM micrographs of the multicomponent interposed carbon nanotube micropatterns with non-aligned carbon nanotubes region-specifically adsorbed between aligned carbon nanotube patterns. (a) a low magnification image, (b) a high magnification image, showing individual adsorbed carbon nanotubes within the hexagonal regions of Fig. 2a.

3. Template-free electrodeposition of interposed metal nanoparticles for carbon nanotube growth

More recently, we have carried out the *template-free* electrodeposition of cobalt (nickel) nanoparticles by applying an AC voltage across an aluminum working electrode and graphite (nickel foil) counter electrode in a two-electrode electrochemical cell containing an aqueous solution of 0.4M H_3BO_3 and 0.3M $CoSO_4$ (0.3M $NiSO_4$). Figs. 3a&b show typical atomic force microscopic, AFM, images for the Ni and Co nanoparticles electrodeposited at 4.0V for 1min and 6.5V for 15s, respectively. In both of the AFM images, a homogenous coverage of spherical nanoparticles with a diameter in the range of 45-50 nm is clearly evident. As can be seen in Fig. 3a, nickel nanoparticles were even deposited into the pits or small holes, which were formed by removal of impurities from the aluminum surface through electropolishing.

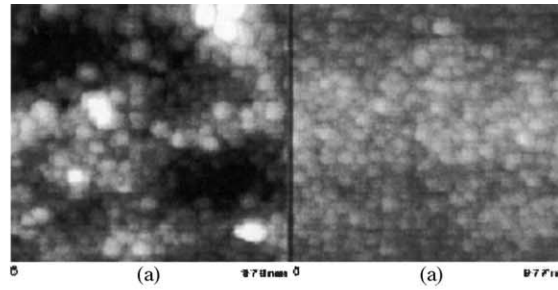
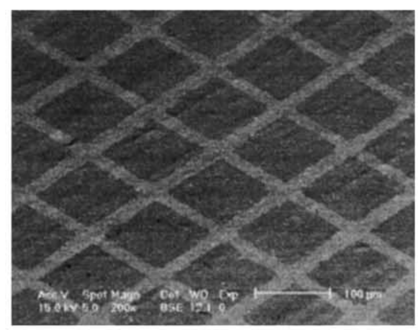


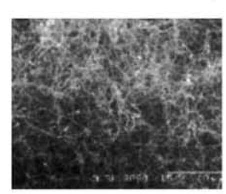
Fig. 3. AFM images of nickel nanoparticles electrodeposited at AC 4.0V for 1min (a), and cobalt nanoparticles electrodeposited at 6.5V for 15s (b).

The well defined metal nanoparticles produced by the aforementioned template-free electrodeposition, together with the ease with which the multicomponent interposed metal micropatterns could be prepared by sequential template-free electroplating of different metal nanoparticles onto a conducting substrate in a region-specific fashion, suggests a wide range of potential applications for the resultant metal nanoparticles to support patterned growth of carbon nanotubes (Fig. 4).

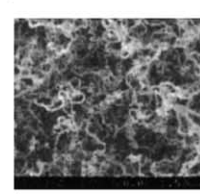


(a)

(b)



(c)

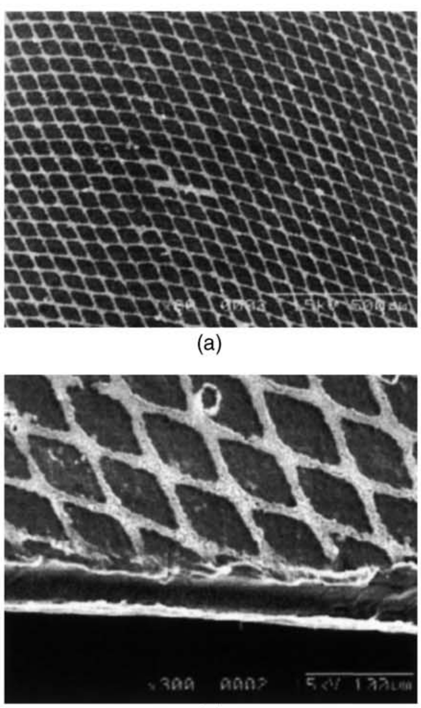


(d)

Fig. 4. SEM images: (a) Back scattering image; the darker square area was electrodeposited with cobalt while the light line area was covered with nickel. (b) carbon nanotubes grown over the substrate interposed with cobalt and nickel nanoplarticles. (c) carbon nanotubes grown over nickel nanoparticles. (d) carbon nanotubes grown over cobalt nanoparticles.

4. Flexible polymer films interposed with aligned carbon nanotube micropatterns

Based on the above work on multicomponent micropatterning of carbon nanotubes, we have also demonstrated that flexible polymer thin films with interdispersed aligned carbon nanotube networks can be prepared, for example, by first patterning *aligned* carbon nanotubes through a region-specific transfer of a non-patterned aligned carbon nanotube film with a Scotch tape pre-patterned with a non-adhesive layer [15]. This was then followed by spin-casting of a polymer (*e.g.* polydiene rubber) solution onto the aligned carbon nanotube network, which was eventually peeled off together with the polymer film from the quartz substrate in a dry state. The resulting polymer film is *flexible* and the interposed aligned carbon nanotube network is clearly evident, as shown in Fig. 5. In view of the good electronic/optical properties characteristic of carbon nanotubes and processability/flexibility associated with most polymers, this dry contact transfer method should enable us to produce flexible polymer and carbon nanotube nanocomposite films for potential applications in novel optoelectronic devices.



(a) (b)

Fig. 5. SEM images of (a) aligned carbon nanotube network interdispersed in a polydiene film and (b) the same as (a), but under a higher magnification, showing aligned carbon nanotube micropatterns dispersed within a polydiene matrix.

5. Conclusion

We have developed several simple, but very effective, methods for producing multi-component interposed carbon nanotube micropatterns by either dry contact transferring preformed carbon nanotubes or template-free electrodepositing micropatterns of metal nanoparticles for nanotube growth. Using the aforementioned methods, we have also successfully prepared flexible nanocomposite polymer films with interposed carbon nanotube networks. Due to the generic nature characteristic of the dry contact transfer and the templat-free electrodeposition of various metallic and nonmetallic (*e.g.* conducting polymers) species, these newly-developed methodologies could be regarded as general approaches toward the construction of multicomponent and multifunctional nanomaterials and nanodevices for a wide range of potential applications.

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